Concept of the H(δ+) ··· H(δ−) Interaction. A Low-temperature Neutron Diffraction Study of *cis*-[IrH(OH)(PMe$_3$)$_4$]PF$_6$†

Raymond C. Stevens and Robert Bau *
Department of Chemistry, University of Southern California, Los Angeles, California 90089, U.S.A.
David Milstein * **and Ofer Blum**
Department of Organic Chemistry, The Weizmann Institute of Science, Rehovot 76100, Israel
Thomas F. Koetzle *
Chemistry Department, Brookhaven National Laboratory, Upton, New York 11973, U.S.A.

The structure of the rare hydridohydroxy complex *cis*-[IrH(OH)(PMe$_3$)$_4$]PF$_6$ has been analyzed at 20 K by single-crystal neutron diffraction. The results confirm the geometry derived from an earlier *X*-ray analysis. Perhaps the most significant result concerns the bending of the O–H group towards the hydride ligand, with a smaller-than-usual Ir–O–H angle of 104.4(7)°, suggestive of an attractive interaction between the electron-deficient H atom of the hydroxy group and the electronegative hydride ligand.

The remarkable ability of the cationic complex [Ir(PMe$_3$)$_4$]$^+$ [1] to partake in oxidative-addition reactions that cleave O–H and S–H bonds, such as the addition of H$_2$S to yield *cis*-[IrH(SH)(PMe$_3$)$_4$]$^+$ and the addition of MeOH to give *cis*-[IrH(OMe)(PMe$_3$)$_4$]$^+$, has enabled this 16-electron iridium(I) species to serve as an efficient 'water-activation' reagent to yield a stable hydridohydroxy complex, [IrH(OH)(PMe$_3$)$_4$]$^+$.[2] Mononuclear hydridohydroxy complexes constitute a rare class of compounds that are strongly implicated in activation–photodissociation of water, water-gas shift reactions, and a large number of other important processes.[3–5] Some complexes of this class have been isolated, but most have been shown either to dimerize or to be unstable in the absence of excess of water.

Recently one of us (D.M.) reported the preparation and first *X*-ray structure determination of an unusually stable mononuclear hydridohydroxy complex *cis*-[IrH(OH)(PMe$_3$)$_4$]PF$_6$.[2] We now describe a neutron diffraction study of this rare complex, an analysis which confirms the results of the earlier *X*-ray work and provides more precise positions for the H atoms.

Experimental

Synthesis and Crystallization.—The complex *cis*-[IrH(OH)(PMe$_3$)$_4$]PF$_6$, M = 659.51, is readily prepared by the addition of water to the unsaturated species [Ir(PMe$_3$)$_4$]PF$_6$.[1] To a red suspension of [Ir(PMe$_3$)$_4$]PF$_6$ (300 mg) in tetrahydrofuran(thf) (2 cm^3) under argon, purified water (300 μl) was added dropwise, forming a yellow solution which becomes colourless after 5 h. The solvent was removed under high vacuum and the resulting white solid washed with a small amount of cold thf to yield pure *cis*-[IrH(OH)(PMe$_3$)$_4$]PF$_6$. I.r. (Nujol): 3 620 (O–H) and 2 068 cm^{-1} (Ir–H). The ^{31}P-{^{1}H} n.m.r. spectrum (in C$_5$D$_5$N) establishes the *cis* configuration of the octahedral complex, showing a doublet of doublets at δ −41.92 (J_1 = 20, J_2 = 16 Hz) for the two equivalent phosphines, a doublet of triplets at −53.93 (J_1 = 16, J_2 = 12 Hz) for the phosphine *trans* to the OH ligand, and a doublet of triplets at −47.94 p.p.m. (J_1 = 12, J_2 = 20 Hz) for the phosphine *trans* to the hydride. The identity of these phosphines was established by proton-coupled ^{31}P n.m.r. spectroscopy, which showed that the signal at −47.94 p.p.m. is split by the hydride into two multiplets with J(P–H) = 157 Hz. The ^{1}H n.m.r. spectrum (in C$_5$D$_5$N) confirmed this assignment, showing a doublet of quartets at −11.19 [J(P–H) = 147 (*trans*), 19 Hz (*cis*)] for Ir–H in addition to a broad singlet for the OH ligand at −1.40, which disappears upon D$_2$O addition. The methyl groups on the *trans* phosphines are virtually coupled to the two phosphorus nuclei, appearing as a triplet at δ 1.61 (J = 3.9 Hz). The two other phosphines give rise to doublets at δ 1.62 (J = 9) and 1.46 (J = 8 Hz). The ^{1}H n.m.r. spectrum in [^{2}H$_8$]tetrahydrofuran is essentially the same, except for the absence of a signal for OH: δ 1.71 (d, J =9.8, 9 H), 1.68 (t, J = 3.5, 18 H), 1.55 (d, J = 8.3, 9 H), and −11.12 (dq, J_1 = 145.8, J_2 = 18.4 Hz, 1 H).

Large crystals for neutron diffraction analysis were grown by room-temperature vapour diffusion of benzene into a solution of the complex (100 mg) in thf (10 cm^3) containing water (10 μl), over a period of 2 d.

Neutron Diffraction Analysis.—A crystal of clear appearance and with approximate dimensions 2.5 × 2.0 × 1.0 mm was covered in a coating of HaloCarbon grease, which also served as mounting adhesive, placed on an aluminium pin oriented approximately along the a^* direction, and enclosed in a specially adapted closed-cycle helium-refrigerator (Air Products and Chemicals, Displex model CS-202). Neutron diffraction data were collected at 20 K on an automated four-circle diffractometer[6] at the Brookhaven High Flux Beam Reactor, using a Ge(220)-monochromated neutron beam of wavelength 1.15930(12) Å, based on KBr, a_o = 6.6000 at 298 K. One reflection (0 2 0) was monitored during cooling (298 to 20 K) and no unusual variation in its intensity was observed. Crystal data are listed in Table 1.

Intensities were measured over one octant of reciprocal space, by means of a θ–2θ step-scan technique, with data being accumulated at each point for a predetermined monitor count of the incident neutron beam. The collection of low-angle ($5 < 2\theta < 60°$) data was completed with a fixed scan width in 2θ of 3.2° and 80 steps per scan. For the high-angle ($60 < 2\theta < 105°$) data a variable scan was used with width ranging from 3.2° for 2θ = 60° to 6.49° for 2θ = 105°, and the step size adjusted to yield between 60 and 90 steps per scan. The high-angle reflections selected for measurement were those predicted to have the largest neutron intensity (model used

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† *cis*-Hydridohydroxotetrakis(trimethylphosphine)iridium(III) hexafluorophosphate.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

Table 1. Summary of crystal data and refinement results for *cis*-$[IrH(OH)(PMe_3)_4]PF_6$ from the neutron diffraction study at 20 K

Space group	*Pnma*
a/Å	14.406(3)
b/Å	11.991(3)
c/Å	13.508(3)
U/Å^3	2 333.4
D_c/g cm^{-3}	1.877
μ/cm^{-1}	3.468
sin θ/λ limit/Å^{-1}	0.6846
Total number of reflections measured	2 586
No. of independent reflections	2 443
No. of reflections used in structural analysis [$F > 4\sigma(F)$]	790
No. of variable parameters	164
R	0.076
R'	0.089

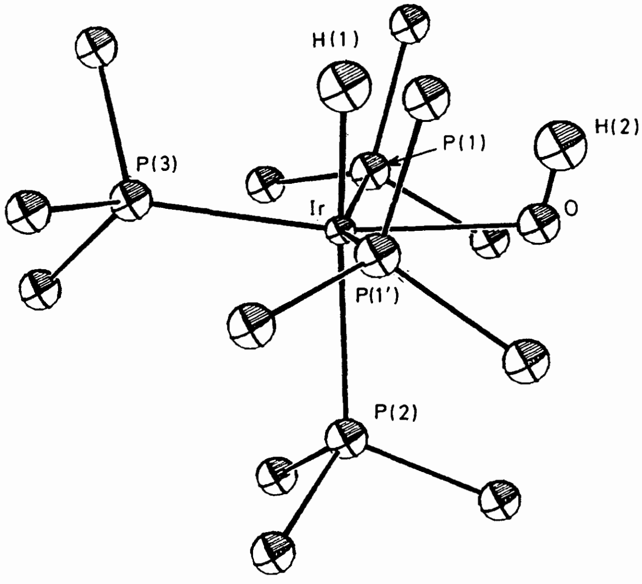

Figure 1. The *cis*-$[IrH(OH)(PMe_3)_4]^+$ cation viewed in the plane of the hydride and hydroxy ligands. Note the pronounced bending of the P(1)–Ir–P(1′) angle toward the OH group. Thermal ellipsoids are drawn by ORTEP[12]

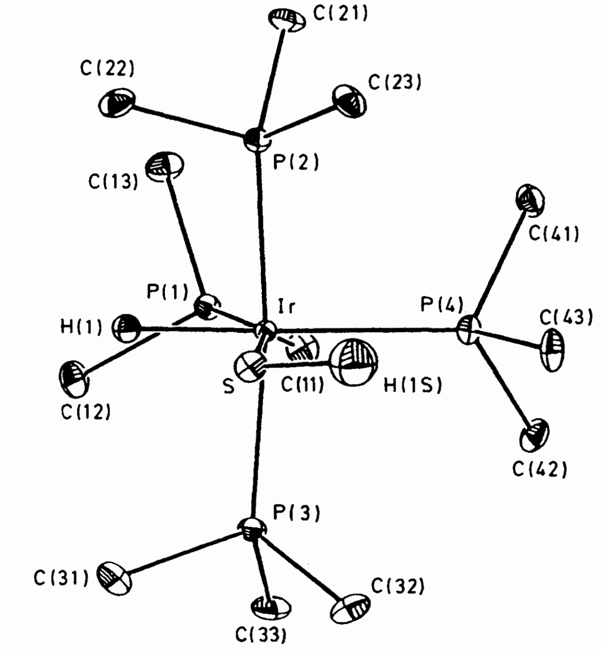

Figure 2. Structure of *cis*-$[IrH(SH)(PMe_3)_4]^+$ (from ref. 2)

based on neutron structure, $2\theta < 60°$),[7] with data collection being terminated when very few of the remaining reflections were observed above background. A total number of 2 586 reflections were recorded. Two intense reflections [(4 5 – 5) and (0 8 0)] were monitored at 200-reflection intervals and no significant variations in their intensities were observed. The step-scan intensity profiles were integrated and background corrections applied based on the counts of approximately seven steps at either end of each scan. The squared observed structure factor and standard deviation for each reflection were obtained upon applying Lorentz and absorption corrections. The latter was calculated by numerical integration over a Gaussian grid of 288 sampling points, with values for the transmission coefficients ranging from 0.531 to 0.680. Averaging Friedel pairs yielded data for 2 443 independent reflections with an unweighted internal agreement factor of $R_{int} = 0.038$. Co-ordinates of the non-hydrogen atoms were obtained from the earlier *X*-ray analysis,[2] and the hydrogen atoms were located from successive Fourier-difference maps. Differential synthesis was used in the initial stages of refinement until all hydrogen atoms were located. Several cycles of refinement, in which positional and isotropic thermal parameters were varied, were then performed. No extinction correction was deemed necessary. The model was refined with full-matrix least squares until convergence was obtained at an R value (on F) of 0.076 and weighted $R(F)$ of 0.089, for 164 variable parameters. A final difference map was noisy but with no interpretable features.

Neutron scattering lengths were taken from a compilation of Koester.[8] Computer programs employed include DIFSYN[9] (differential synthesis), a modified version of SHELX 76[10] (full-matrix least-squares program), the absorption correction procedure of Coppens *et al.*,[11] C. K. Johnson's ORTEP 2,[12] and locally written programs.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond distances and angles.

Results and Discussion

A view of the *cis*-$[IrH(OH)(PMe_3)_4]^+$ cation is shown in Figure 1; crystal data and refinement results are given in Table 1, final atomic parameters in Table 2, and selected distances and angles in Table 3. The structure is essentially the same as that found in the *X*-ray analysis,[2] with more precise H-atom positions, as mentioned earlier. Both the cation and anion are situated on a mirror plane. For the cation, this plane is defined by Ir, the OH ligand, the hydride ligand, and atoms P(2), P(3), and C(21), while that for the anion passes through the P and four F atoms. In the cation, the P(3) PMe_3 ligand is disordered as was found to be the case in the *X*-ray structure determination. In view of the disorder, and the relatively small number of reflections with intensities significantly above background, it was decided to refine all atoms with isotropic thermal parameters.

The Ir–O–H angle determined by neutron diffraction [104.4(7)°] is larger than that of 91(7)° measured from the *X*-ray analysis, but remains significantly smaller than the normal tetrahedral value of 109.5°. The Ir–P distance *trans* to the hydride ligand [Ir–P(2) 2.364(6) Å], is significantly larger than that *trans* to the hydroxy ligand [Ir–P(3) 2.265(6) Å]. As noted earlier,[2] this is consistent with H having a larger *trans* influence than OH. The Ir–H bond distance [1.617(9) Å] lies within the

Table 2. Final atomic parameters for *cis*-$[IrH(OH)(PMe_3)_4]PF_6$ from the neutron diffraction study at 20 K

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ir	0.233 8(4)	0.2500	0.148 3(5)	H(13B)	0.319 5(12)	0.038 3(16)	−0.020 0(13)
O	0.365 9(7)	0.2500	0.221 6(8)	H(13C)	0.408 9(13)	0.074 2(17)	0.061 7(14)
H(1)	0.292 5(13)	0.2500	0.046 9(16)	H(21A)	0.281 1(12)	0.175 2(17)	0.409 2(13)
H(2)	0.407 6(18)	0.2500	0.171 7(20)	H(21B)	0.197 2(17)	0.2500	0.481 1(18)
P(1)	0.261 7(6)	0.058 1(7)	0.146 1(7)	H(22A)	0.116 8(10)	0.445 6(13)	0.329 3(12)
P(2)	0.158 0(8)	0.2500	0.303 5(8)	H(22B)	0.023 6(11)	0.372 6(13)	0.277 6(11)
P(3)	0.109 4(11)	0.2500	0.047 4(13)	H(22C)	0.053 4(11)	0.360 0(16)	0.406 7(13)
C(11)	0.174 0(6)	−0.049 7(8)	0.129 1(6)	H(31A)	0.073 6(25)	0.170 6(33)	0.882 1(26)
C(12)	0.317 2(5)	0.006 9(7)	0.260 0(6)	H(31B)	0.159 1(35)	0.094 5(43)	0.941 2(35)
C(13)	0.347 0(5)	0.023 7(6)	0.053 1(5)	H(31C)	0.192 0(24)	0.226 9(33)	0.890 7(26)
C(21)	0.235 8(6)	0.2500	0.411 4(6)	H(32A)	0.015 6(25)	0.087 7(30)	0.112 0(27)
C(22)	0.081 5(4)	0.367 7(6)	0.332 4(5)	H(32B)	−0.045 3(23)	0.170 2(32)	0.025 8(26)
C(31)	0.137 3(12)	0.178 2(17)	−0.069 7(13)	H(32C)	−0.031 5(21)	0.221 6(23)	0.142 5(23)
C(32)	0.003 8(11)	0.181 1(16)	0.084 6(13)	H(33A)	0.004 8(22)	0.142 9(31)	0.950 0(25)
C(33)	0.058 0(11)	0.121 1(16)	0.000 2(13)	H(33B)	0.034 1(19)	0.070 6(25)	0.059 3(21)
H(11A)	0.117 8(13)	0.959 0(18)	0.182 5(14)	H(33C)	0.118 5(29)	0.069 3(38)	−0.037 1(30)
H(11B)	0.147 0(17)	0.954 3(22)	0.049 5(21)	P(4)	0.475 0(8)	0.2500	−0.164 0(9)
H(11C)	0.206 0(18)	0.866 3(25)	0.137 7(19)	F(1)	0.473 1(7)	0.382 5(9)	−0.161 4(8)
H(12A)	0.265 9(12)	−0.002 1(14)	0.319 1(12)	F(2)	0.587 0(9)	0.2500	−0.174 7(10)
H(12B)	0.366 6(12)	0.070 7(16)	0.286 6(14)	F(3)	0.363 2(10)	0.2500	−0.150 8(12)
H(12C)	0.347 5(13)	−0.076 7(17)	0.246 5(14)	F(4)	0.485 7(8)	0.2500	−0.044 4(10)
H(13A)	0.367 4(12)	−0.065 4(16)	0.058 4(13)	F(5)	0.463 2(9)	0.2500	−0.282 9(11)

Table 3. Selected bond distances (Å) and angles (°) in *cis*-$[IrH(OH)(PMe_3)_4]PF_6$

Ir–H(1)	1.617(9)	P–C(mean)	1.822(6)
Ir–O	2.119(5)	C–H(mean)	1.089(8)
Ir–P(1)	2.338(4)	P–F(mean)	1.607(7)
Ir–P(2)	2.364(6)	O–H(2)	0.93(1)
Ir–P(3)	2.265(6)	H(1) ··· H(2)	2.40(1)
Ir–O–H(2)	104.4(7)	P(2)–Ir–P(3)	100.0(2)
O–Ir–H(1)	87.8(4)	P(1)–Ir–H(1)	84.4(1)
P(3)–Ir–H(1)	82.0(4)	P(1)–Ir–O	81.1(1)
P(3)–Ir–O	169.8(2)	P(1)–Ir–P(3)	97.8(1)
P(2)–Ir–H(1)	178.0(4)	P(1)–Ir–P(2)	95.3(1)
P(2)–Ir–O	90.2(2)	P(1)–Ir–P(1′)	159.2(2)
Ir–P–C(mean)	116.6(2)	H–C–H(mean)	108.7(9)
P–C–H(mean)	110.2(8)		

range of reported[13–16] neutron values for terminal Ir–H of 1.586(3)—1.627(4) Å.

Perhaps the most significant features of the structure of *cis*-$[IrH(OH)(PMe_3)_4]^+$ can be summed up as follows: (*i*) a comparison with the structure of *cis*-$[IrH(SH)(PMe_3)_4]^+$ (Figure 2) shows the O–H group pointing *towards* the hydride ligand, while in the sulphur analogue the S–H group is pointing *away* from the H ligand;[2] (*ii*) as mentioned before, the Ir–O–H angle is significantly smaller than the normal tetrahedral value, as opposed to 111(3)° in the complex mentioned above or 119.4(9)° in the analogous complex *cis*-$[IrH(OMe)(PMe_3)_4]PF_6$.[2] These two values are based on the *X*-ray analysis; neutron diffraction may yield slightly different results.

Both of these observations can be rationalized by postulating an attractive interaction between the hydridic Ir–H and the electron-deficient OH proton, in effect an H(δ+) ··· H(δ−) interaction (Ir–H ··· H–O). The sulphur atom, being both bigger and less electronegative than oxygen, does not encourage such an interaction. The present compound does not show the expected intermolecular hydrogen bonding involving the OH group, consistent with the presence of the intramolecular interaction mentioned above. Although the spectroscopic data are not necessarily indicative of such an interaction and the observed OH ··· H distance of 2.40(1) Å is too long for the interaction to be considered a normal hydrogen bond, studies are currently underway with a view towards synthesizing compounds whose geometries might lend themselves more favourably towards a true H(δ+) ··· H(δ−) interaction.

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